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PERSONNEL

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ELECTROCALORIC MEASUREMENTS OF TARTARIC ACID

A pyroelectric substance can be thought of as a ferroelectric substance whose spontaneous polarization though dependent upon temperature and electric field, cannot be reversed by an electric field. For purposes of measuring its electrocaloric effect, a pyroelectric crystal can be regarded as being self-biased to a large initial value of polarization; i.e., to a state analogous to those in the thermodynamically reversible tail of a hysteresis cycle.

For a complete analysis of the electrocaloric effect exhibited by any substance, one needs, besides the electrocaloric measurements themselves, the specific heat $c_p(T)$ and the spontaneous polarization $P_s(T)$ of the substance as functions of temperature. We have made the desired electrocaloric measurements of a pyroelectric crystal (tartaric acid) but they will not be discussed until we have obtained data for the specific heat, probably from another laboratory; published values are averages over wide ranges of temperature or values for a few selected temperatures. Our attempts to measure $P_s(T)$ for tartaric acid are described in the next section.

THERMAL DEPOLARIZATION OF TRIGLYCINE SULFATE AND TARTARIC ACID

The spontaneous polarization of tartaric acid cannot be reversed by an electric field, so the usual method of determining $P_s(T)$ from the hysteresis cycle fails. The only published value that we have found for the spontaneous polarization of a pyroelectric crystal is Voigt's estimated lower limit of 33 esu/cm ($0.11 \text{ millicoul/m}^2$) cited by Cady¹ for tourmaline at 24°C . Voigt obtained this value

by cleaving a crystal perpendicular to its pyroelectric axis and immersing the two parts in cups of mercury that were connected to an electrometer. This method is subject to much error.

Thermally induced changes in P_s can be determined by integrating the "thermal depolarization current", the current that flows when a short-circuited crystal is heated or cooled. In principle, if the crystal is heated until P_s is reduced to zero, the value of P_s as a function of temperature can be determined. Unfortunately, there is no way to know from external measurements whether P_s really disappears or is masked by internal conductivity as the temperature is raised. Moreover, the true thermal depolarization current can be mingled with currents arising from excessive temperature gradients (so-called tertiary pyroelectricity¹) or by internal migration of space charge caused by previously applied fields, for example a field that may have been generated by the crystal's own pyroelectric effect.

To test its validity, the method of determining $P_s(T)$ from measurements of thermal depolarization currents was tried on triglycine sulfate (TGS) for which $P_s(T)$ is known from both hysteresis and electrocaloric measurements.^{2,3}

Experimental Method

At "higher" temperatures where our Wood's-metal vacuum seals might fail, the apparatus represented by Fig. 1 (with the necessary electrostatic shields omitted) was used. The field applied to the crystal was kept at a negligible value either by using the electrometer in its feed-back mode or by adjusting the compensating circuit. Except for tartaric acid crystals at temperatures above 398°K, these

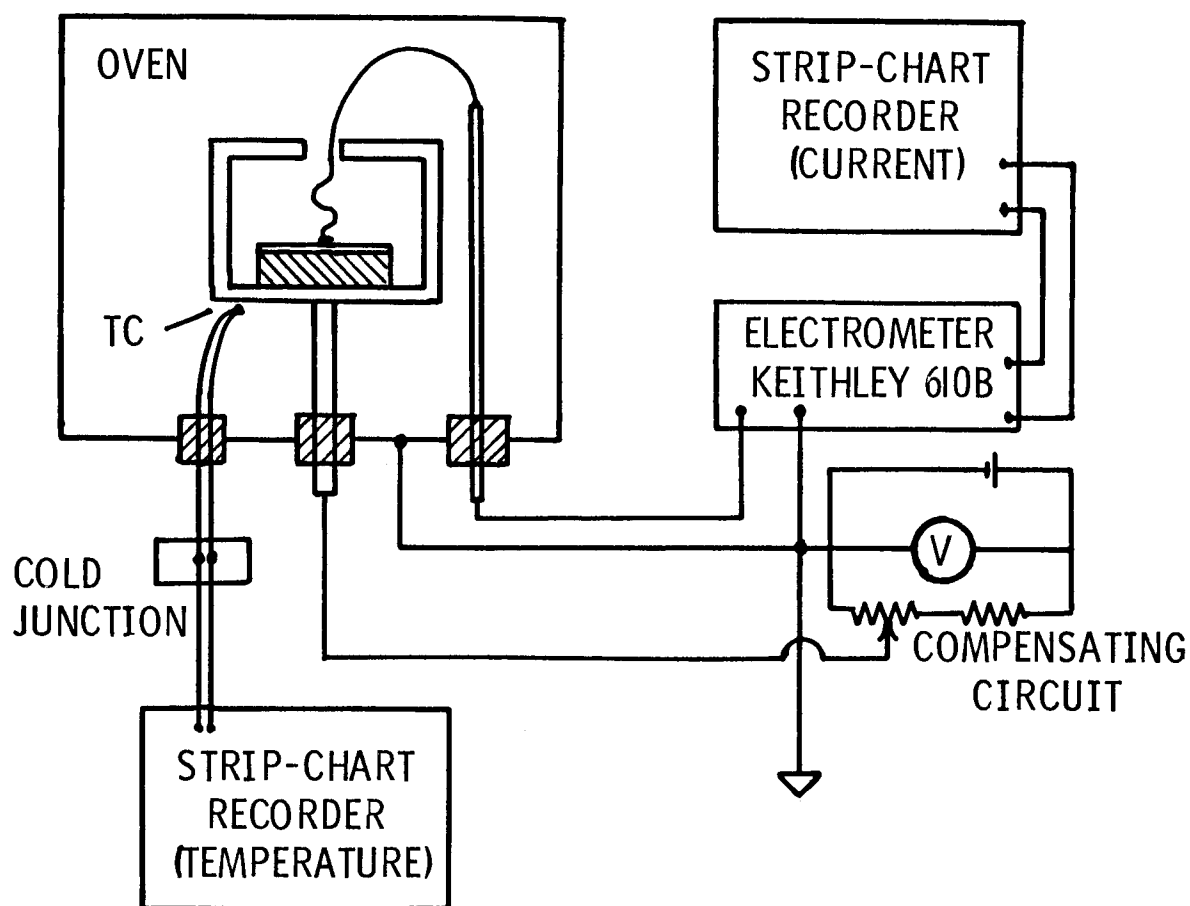


FIG. 1 APPARATUS FOR MEASURING THERMAL DEPOLARIZATION CURRENTS AT HIGHER TEMPERATURES

precautions were found to be unnecessary since full compensation produces a maximum change of only 1% in the measured current.

The rate of temperature rise was controlled crudely by a motor-driven thermostat; cooling was uncontrolled -- the oven was merely turned off. In all cases the temperature of the crystal was monitored by a strip-chart recorder.

At lower temperatures, the crystal chamber described in our Report No. 2⁴ was used except that the Keithley Model 610B electrometer replaced the breaker amplifier q and capacitor C_D shown in Fig. 2 of that report. Various coolants placed in the dewar which surrounds this apparatus caused the desired changes in temperature.

Measurements of Triglycine Sulfate (TGS)

Preliminary experiments were performed with TGS crystals grown in this laboratory. The following observations can be made about these experiments:

- (1) Inverting the crystal in its holder and then making otherwise identical measurements of the thermal depolarization current showed that unwanted thermal gradients did not generate spurious currents.
- (2) Eight-fold variations in heating or cooling rate did not give a significant change in the observed values of $P_s(T)$.
- (3) Replacing the silver paste electrodes by goldleaf electrodes gave no significant change in the observed values of $P_s(T)$.
- (4) Prior cooling of the specimen from 448°K to room temperature with an electric field applied left no residual charges to spoil the measurements of $P_s(T)$.

- (5) The polarization as measured by this method can be changed in sign by the application of a field below the Curie temperature whereas it cannot be changed by a field applied above the Curie temperature; i.e., temporarily heating a previously-polarized crystal above T_c caused it to revert to a preferred polarity which was evidently established when the crystal was grown.
- (6) Heating a crystal which had been previously polarized oppositely to its preferred polarity would when heated begin to depolarize (about 2° too low) first in the direction expected from its preferred polarity and then in a direction consistent with the polarizing field. This effect is consistent with the asymmetry previously observed in the hysteresis loops of crystalline TGS.³
- (7) Cooling and heating gave quantitatively reversible changes in polarization unless the effect noticed in (6) above was occurring.

Depolarization measurements made with the same TGS crystal that was used in the electrocaloric measurements³ yielded a value of $28.3 \text{ millicoul/m}^2$ for P_s at 303°K , a value that is identical to the value obtained from the electrocaloric measurements. The observed values of the critical temperature are not accurate; they varied between 321.0°K and 323.2°K as compared to 322.60°K obtained by the electrocaloric method.

In view of the tests cited, we believe that the method of thermal depolarization is an accurate way to measure $P_s(T)$, at least

accurately enough so that comparable measurements of a pyroelectric substance should be taken seriously.

Measurements of Tartaric Acid

Crystals grown in this laboratory by evaporation from water solution, and a crystal grown by Clevite gave equivalent results. Some properties of crystalline tartaric acid are given below:

Formula :	d-form $C_4H_6O_6$
Size of crystals:	approx. 1.5 cm^2 by 2 mm.
Density:	1.760 g/cm^3 .
Crystal symmetry:	Monoclinic
Pyroelectric axis:	Along $[110]$

The laboratory-grown crystals were water polished and given a light sanding to remove etch pits, and then electrodes of silver paste were applied to their entire major surfaces.

The Clevite specimen was used just as it was prepared for the electrocaloric measurements.

The thermal depolarization currents from virgin specimens of tartaric acid are like those expected from any crystal such as TGS which undergoes a second-order phase transition. The transition temperature is taken as the temperature at which the depolarization current goes to zero while the temperature of the crystal is still rising. Values of $P_s(T)$ that were obtained by integrating the depolarization current as one typical specimen was heated from 298°K to 413°K are shown in the right-hand portion of Fig. 2.

Except for variations of about $\pm 3^{\circ}\text{K}$ in the transition temperature, all virgin crystals give nearly the same values for $P_s(T)$; moreover their polarization is quantitatively reversible with respect to temperature provided that the crystals are not heated too close to the transition temperature. Overheating increases or decreases the transition temperature by an unpredictable amount, sometimes ten or fifteen degrees. Above the transition, thermally stimulated current occurs, but not even its direction is predictable; moreover, exceeding the transition temperature causes the surface of the crystal to become slightly sticky and bumpy.

The erratic behavior of crystalline tartaric acid near its transition temperature prevented us from obtaining precise values of $P_s(T)$. On the other hand, all crystals gave consistent values for $P_s(T)$ below 396°K , and in no crystal did the apparent transition temperature occur below this temperature.

Fig. 2 represents a combination of the thermal depolarization measurements on two virgin samples. One was heated from 298°K through its transition temperature, and the other was cooled from 328.9°K to 108.4°K . The latter crystal was the same one on which electrocaloric measurements (not yet reported) were made. The two sets of data were fitted at 305.2°K . Comparison of Fig. 2 with the well-known behavior of ferroelectric substances reveals the expected qualitative similarity between $P_s(T)$ for pyroelectric tartaric acid and ferroelectric triglycine sulfate or, for that matter, any ferroelectric substance which undergoes a second-order transition. We believe that the values shown in Fig. 2 represent more nearly the internal polarization of tartaric acid than do the much smaller

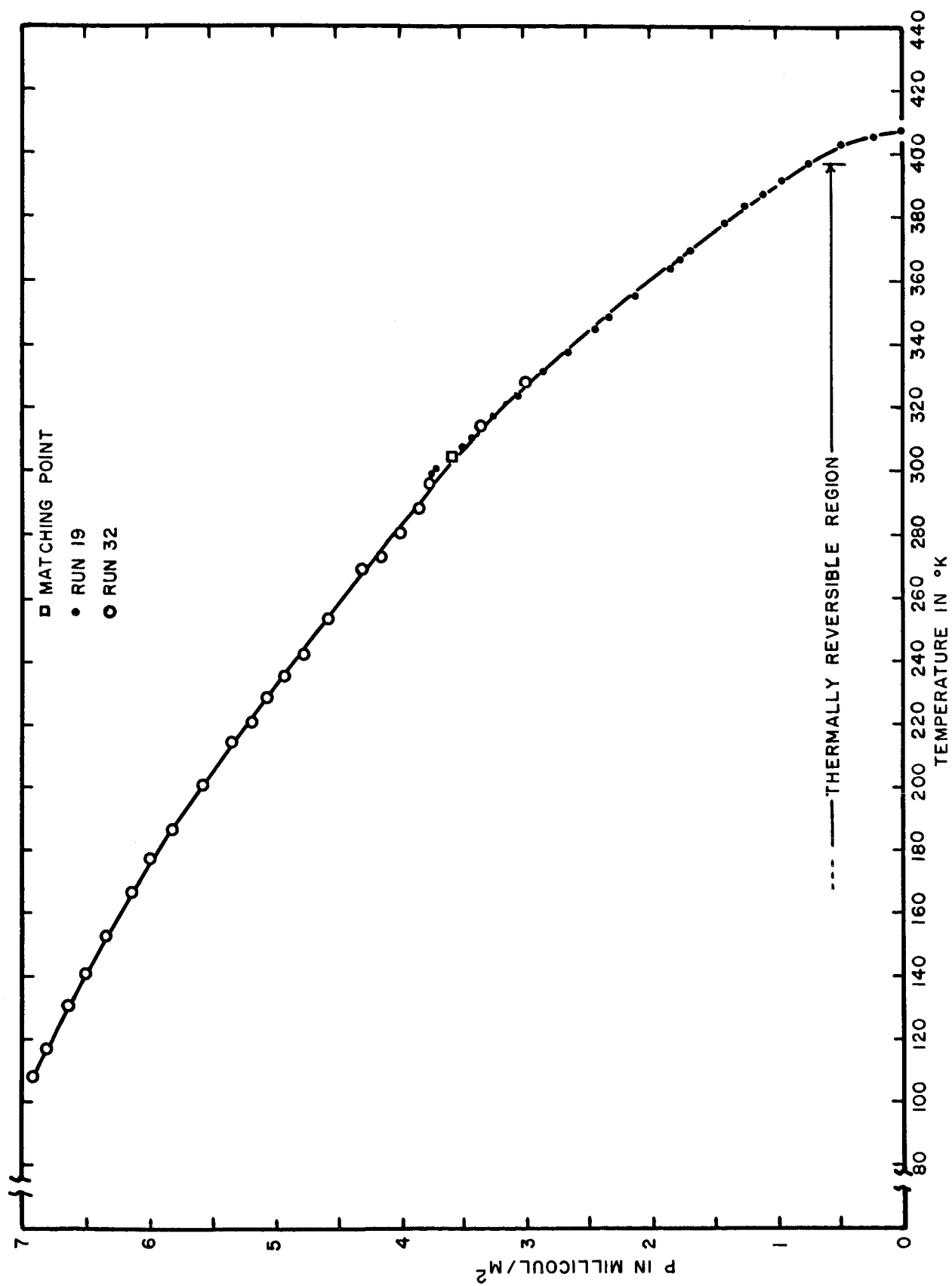


FIG. 2 INTRINSIC POLARIZATION OF TARTARIC ACID

values previously published for similar substances. Our values, if in error, are more likely to be too low than too high.

The pyroelectric coefficient for a short-circuited, unstressed crystal is given by the expression⁵

$$p^{X,E} = (\partial P / \partial T)_{X,E} \quad (20)$$

so the pyroelectric coefficient of tartaric acid is the slope of Fig. 2. Its value as a function of temperature is shown in Fig. 3.

Comparison of the pyroelectric coefficient to the electrocaloric data and the use of these data to evaluate tartaric acid as a radiation detector require data for the specific heat as a function of temperature; these data are not yet available. However, our low-temperature test chamber, though not suitable for measuring specific heat, is well-suited for detecting anomalies in the specific heat. The method of detection consists of cooling or heating the whole apparatus slowly while measuring the temperature difference between the mounted crystal and the massive copper chamber that surrounds it, a method that we employed previously.⁶ This method revealed no anomalies in the specific heat of tartaric acid between 104°K and 330°K even though it was sensitive enough to detect the thermal disturbance resulting from a small chipping of the crystal that occurred at 232°K while the crystal was being reheated to room temperature. The absence of an anomaly in the specific heat in conjunction with the measured values of $P_s(T)$ means that the electrocaloric effect should be a smooth function of the temperature and that the variation of the pyroelectric coefficient with temperature

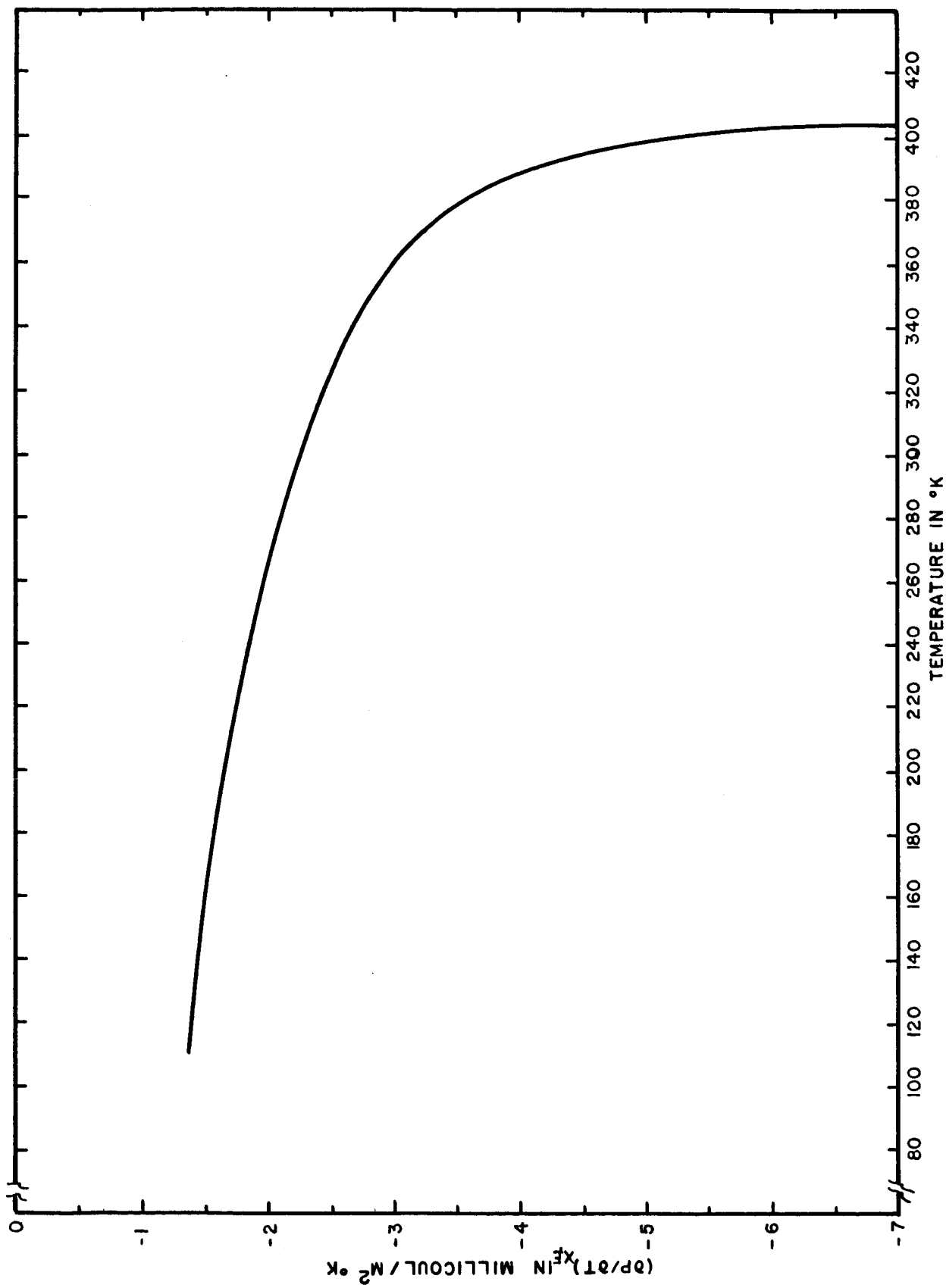


FIG. 3 THE PYROELECTRIC COEFFICIENT OF TARTARIC ACID

as plotted in Fig. 3 gives a good qualitative picture of its sensitivity as a radiation detector.

VACUUM-PLATED VS. SILVER PASTE ELECTRODES

Accounts in the literature¹ and experiments in this laboratory reveal that some types of measurements on ferroelectric substance are affected by the kind of electrodes used. Ohmic contact by the electrodes which is so important in measurements of semiconductors and photoconductors is not important in ferroelectric measurements inasmuch as ferroelectric substances are good insulators. Consequently, the effect of different electrodes is due not to the different metals involved but to differences in the intimacy of contact between the dielectric and the electrode. Lack of intimate contact, which is due to a film of foreign substance, a gap, or the abrupt change in properties near the surface of the dielectric, can be simulated by a pair of gaps which, for the present case, can be lumped into one as shown in Fig. 4.

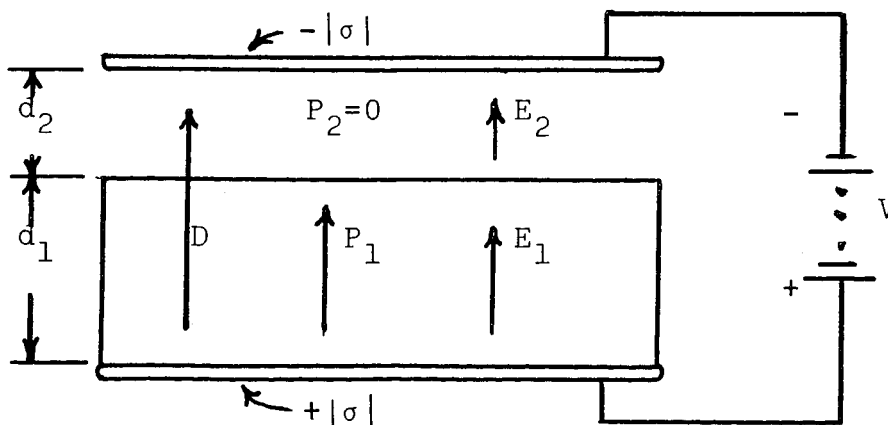


Fig. 4. One Gap d_2 Simulates Imperfect Dielectric-Electrode Contacts. Region 1 represents the dielectric and region 2 represents the gap(s).

Experimentally, the polarization P_1 is computed from measured values of the surface charge density on the electrodes. In rationalized MKS units we can write

$$V_1 = E_1 d_1 + E_2 d_2, \quad (36)$$

$$E_2 = \sigma / \epsilon_0 K_2 \quad (37)$$

and

$$D = \sigma = \epsilon_0 E_1 + P_1.$$

Solving these equations for P_1 gives

$$P_1 = \sigma(1 - d_2/d_1 K_2) - \epsilon_0 V/d_1 \quad (38)$$

so, at first thought, σ seems to be an accurate measure of P_1 even in the presence of a reasonably-sized gap d_2 . What the gap does, however, is to change the observed value of σ by reducing the field in region 1. This effect can be shown by solving Eq. (36) and (37) for E_1 and replacing σ by $\epsilon_0 K_1 E_1$; this gives

$$E_1 = V (d_1 + K_1 d_2/K_2). \quad (39)$$

In the case of a ferroelectric substance whence $K_1 \gg K_2$, the error arising from the gap can be large; for example, K_2 for KH_2PO_4 can be as large as 100,000.

Successive observations of 60-cps hysteresis loops were made on a single specimen to which had been applied in turn electrodes of silver paste, vacuum-evaporated metal, and then (in some cases) silver paste again. Several single-crystal specimens of triglycine sulfate (large value of K_2) and tartaric acid (small value of K_2)

were used. The evaporated metal was gold or indium.

As a result of these measurements, the following conclusions are drawn. (1) Indium adheres better than gold, but it tends to diffuse into clumps after several weeks in air leaving sparsely-covered regions between the clumps, (2) Cleaning the specimens successively in 1-1-1 trichloroethane, ethanol, and distilled water before vacuum plating gives significantly better results, and adhesion than vacuum plating onto a freshly-sanded surface. (3) For TGS, evaporated metal electrodes give values for P_s that are 3% to 14% higher than the values obtained for silver paste electrodes. (4) The superiority of the metal electrodes is greater for TGS than for tartaric acid.

SUMMARY

Measurements of the electrocaloric effect were made on single crystals of tartaric acid, but the results are not reported here because the specific heat of this substance as a function of temperature is not yet available.

The method of obtaining $P_s(T)$ by means of thermal depolarization currents was validated by trials with a previously-measured substance, triglycine sulfate. Then the thermal depolarization method was used to obtain $P_s(T)$ of tartaric acid, a substance for which conventional methods for measuring $P_s(T)$ are not feasible. The pyroelectric coefficient of tartaric acid from 104°K to 330°K was computed from the values of $P_s(T)$ so obtained.

Experiments revealed that vacuum-plated metal electrodes give higher (and presumably better) values of polarization than do measure-

ments with metal foil or silver paste electrodes, 3% to 10% higher for triglycine sulfate at 60-cps.

APPENDIX A: DEFINITION OF TERMS AND SYMBOLS

Rationalized MKS units are used throughout. Thermodynamic formulas such as $dU = TdS + Xdx + EdP$ are written for a unit volume of material. This procedure is not exactly proper because the thermodynamic system (the experimental crystal) changes its volume slightly, but only inappreciable errors result.

C = Curie constant. Curie-Weiss Law is $\chi = C/(T - T_p)$.

c_E = Specific heat at constant field (and zero stress).

c_p = Specific heat at constant polarization (and zero stress).

D = Electric displacement. $D = \epsilon_0 E + P$.

E = Applied electric field.

G_1 = Elastic Gibbs function. $G_1 = U - TS - xX$.

$G_{10} = G_1$ at some (arbitrary) reference temperature.

p = Electric dipole moment.

P = Electric polarization per volume. P_S is the spontaneous electric polarization per volume.

P^E = Pyroelectric coefficient at constant field (and stress).

S = Entropy per volume.

T = Temperature in degrees Kelvin.

T_c = Critical temperature (loosely speaking, either T_f or T_p).

T_f = Ferroelectric Curie temperature = the temperature at which P_S disappears when the substance is heated.

T_p = Paraelectric Curie temperature as defined by the Curie-Weiss Law, $\chi = C/(T - T_p)$.

U = Internal energy per volume.

X = Applied stress. (Tensile stress has a positive sign.)

x = Strain. (Elongation has a positive sign.)

ϵ_0 = Electric permittivity of vacuum = 8.85×10^{-12} coul²/n.m².

ζ = Devonshire's sixth-order coefficient (of P^6) in G-expansion.

ξ = Devonshire's fourth-order coefficient (of P^4) in G-expansion.

(ψ appears as a misprint in place of ξ in Eq. 7 and 9 of Status Report No. 1.)

ρ = Mass density.

χ = Electric susceptibility. $dP = \epsilon_0 \chi dE$. The symbol χ may carry subscripts such as p (paraelectric), or superscripts such as T (constant temperature), X (constant stress), etc.

ψ = The non-linear polarization function in the Devonshire expansion.

Usually written $\psi(P)$.

ψ' = The derivative of $\psi(P)$ with respect to P . Usually written $\psi'(P)$.

ω = Devonshire's second-order coefficient (of P^2) in G-expansion.

NOTE: Equations in the two Status Reports are numbered in order beginning with those in Status Report No. 1.

APPENDIX B: SUMMARY OF PREVIOUS STATUS REPORTS

Status Report No. 1 contains a thermodynamic description of the electrocaloric effect, the pyroelectric effect, and the relationship between them. Such a description includes the proposition that both effects arise from the same crystalline properties and that the relevant thermodynamic coefficients can be determined from measurements of the electrocaloric effect. So-called "tertiary effects", which arise from temperature gradients or fields and can be so large that they mask the real effects, are more easily eliminated from the electrocaloric measurements than from the pyroelectric measurements.

The apparatus and techniques that were devised for regulating accurately the temperature of the experimental chamber and for making simultaneous measurements of the changes in electric polarization and temperature that occur with changes in applied field were described.

Status Report No. 2 included an account of the measurements of the electrocaloric effect in KH_2PO_4 over the temperature range from 78°K to 136°K . Numerical values for the pyroelectric coefficient and its variation with temperature were determined from the measured electrocaloric effect. Reliable values for the Devonshire coefficients could not be determined from the electrocaloric effect because their determination depends upon measured values of changes in polarization, and the polarization of KH_2PO_4 is nearly saturated in the nearly-reversible tail of the hysteresis loops where the electrocaloric measurements are valid. (E.g., see Fig. 4 of Status Report No. 2.)

Report No. 3 describes the changes in the apparatus and techniques that were made to permit measurements of changes of polarization in the nearly-reversible tails of the hysteresis loops (i.e., in the "saturation" region). These changes included the use of (1) a well-regulated, high-voltage d-c power supply, (2) a much more sensitive d-c amplifier with a much higher input resistance for measurements of polarization, and (3) a charge-biasing procedure to suppress the zero of the charge-measuring equipment. Measurements of both $\Delta T/\Delta P$ and $\Delta T/\Delta E$ were made for potassium dihydrogen phosphate over the entire temperature range for which the electrocaloric effect is appreciable, 77°K to 136°K. These measurements show that maximum sensitivity for low-impedance pyroelectric detectors used in the ferroelectric state is not obtained until the applied biasing field is sufficiently large to bring the specimen into the nearly-reversible tail of the hysteresis loop. The sensitivity of a pyroelectric detector operated in the paraelectric state, can be controlled over a wide range by a suitable biasing field, the sensitivity increasing with the field.

A relatively simple expression was found which gave a good fit to measured values of $(\Delta T/\Delta P)_S$ for KH_2PO_4 over the entire temperature range, right through the Curie temperature. It is

$$(\partial E/\partial P)_T = (\rho c_p/T)(\Delta T/\Delta P)_S = 3.63 \times 10^7 P - 4.80 \times 10^{12} P^5.$$

On the other hand, a Gibbs function G_1 that accurately describes both the ferroelectric behavior and the pyroelectric coefficient over the entire range of temperature could not be found.

The variation with temperature and field of an inner field

APPENDIX C: LIST OF EQUATIONS

A list of the most important equations from previous reports is given below. Equations are numbered consecutively, as they first appeared in the reports.

$$dU = TdS + Xdx + EdP \quad (1)$$

$$dT = (T/\rho c_p)(\partial E/\partial T)_p dP \quad (2)$$

$$dT = (T/\rho c_E)(\partial P/\partial T)_E dE \quad (4)$$

$$P = f(a) = f[p(E + \gamma P)/kT] \quad (5)$$

$$dT = (\gamma/\rho c_p)PdP \quad (6)$$

$$dG_1 = -SdT - x dX + EdP \quad (7)$$

$$G_1 = G_{10} + \omega P^2/2 + \xi P^4/4 + \zeta P^6/6 \quad (8)$$

$$(\partial G_1/\partial P)_T = E = \omega(T)P + \xi P^3 + \zeta P^5 \quad (9)$$

$$dP = P^{X,E}_{dT} \quad \text{where } p^{X,E} = (\partial P/\partial T)_{X,E}. \quad (20)$$

bubbles which ammonium hydrogen sulfate has acquired because it is very deliquescent. If the material can be dried before it crystallizes, we may be able to grow usable crystals.

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